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Practical plasma immersion ion implantation for stress regulation, treatment of insulators and complex shapes

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Abstract: Plasma immersion ion implantation has been attracting the interest of research groups around the world over the last two decades. The technique has been developed to the stage where it is a well-established technique for a number of materials processing applications, such as plasma nitriding. Recent research has focussed on developing the method for a range of new applications, including stress regulation, surface treatment of insulators and complex shaped workpieces. The state of development of these new and technologically important applications will be discussed in this paper.

1. Introduction

Plasma immersion ion implantation (PIII) was first investigated in the late 1980s as an alternative to extracted ion beams for achieving ion implantation of a workpiece [1,2]. The advantages were identified to be the high flux of impinging ions and the conformal nature of the implantation, which reduced the need to rotate the workpiece during treatment. PIII utilises the application of short, high-voltage pulses to a substrate immersed in a plasma from which ions are drawn across a high voltage sheath and implanted into the substrate surface. As a competitor to beam line methods, PIII also has some disadvantages. These include difficulties accessing very high ion energies due to electric breakdown occurring across the plasma sheath and the larger energy spread of implanted ions, including a considerable proportion of low energy ions. The low ion energies are due to the finite rise and fall times of the high voltage pulse. Recent simulation work on the sheath dynamics has shown that the major low energy ion contribution is due to the pulse rise-time despite the fact that it is usually shorter than the fall-time[3].

PIII can also be applied during film deposition to modify the properties of the film during growth [4,5,6], most importantly the intrinsic stress and preferred orientation or texture. In the first section of this paper we present some of the recent findings of our group pertaining to the reduction of stress in growing films. Although it is straightforward to apply a voltage directly to a conductive workpiece, the treatment of insulators with PIII is complicated by the dielectric response of the workpiece and the build up of charge on its surface during the implantation process. Our recent studies of these phenomena and ways to avoid or reduce their effects are presented in the second section of this paper with a focus on the sheath dynamics. The extent to which a PIII surface treatment is conformal depends on the behaviour of the plasma sheath around it. Difficulties can arise when treating complex shaped workpieces, particularly those with curvatures of small radii such as sharp points or edges. The last section of this paper discusses the sheath behaviour leading to these difficulties.

2. Stress regulation

PIII, when applied during a physical vapour deposition (PVD) process, has been shown to significantly reduce the level of intrinsic stress in the growing film[6]. Our recent experimental results show that this effect is observed in carbon, titanium nitride and aluminium nitride systems (i.e. in all of the materials we have studied to date) deposited using a cathodic arc plasma. Because this group of materials contain a variety of microstructures, including crystalline cubic and hexagonal, as well as amorphous microstructures, we believe that the observed reduction in stress is a universal phenomenon which could be applied to all films deposited using PVD processes. Stress relief is observed for pulse biases exceeding approximately 500 eV in the materials we have studied.

Figure 1 shows the relationship between the pulse voltage – frequency product and the intrinsic stress in thin films of carbon. The pulse length was kept at 20 μs throughout this series of depositions, while the pulse bias was varied between 1.7 and 20 kV. Pulse frequencies of 200, 800 and 1200 Hz were used.

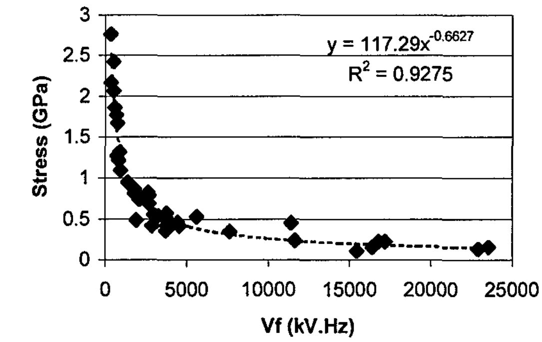

Figure 1: Film stress in cathodic arc deposited carbon treated with PIII during deposition, plotted against the pulse bias voltage-frequency product.

The majority of the points from all data sets (200, 800 and 1200 Hz) lie on a curve given by the fitting function

$y=117.29x^{-0.6627}$, where y is the value of residual stress in GPa and x is the Vf product. The curve shows that when Vf is low, increases in Vf yield large increments of stress relaxation. As Vf increases, increments of stress relief achievable from further increases in Vf are progressively smaller. This can be attributed to the fact that once a significant portion of the film's volume has been treated with *thermal spikes* (small heated volumes surrounding the impact sites of the high energy ions), the effectiveness of subsequent spikes is reduced. As the density of treated surface regions increases, incoming impacts have a non-negligible probability of overlapping with a volume already relaxed by a previous thermal spike. This issue of thermal spike overlap has been discussed in detail and an upper bound for its value has been estimated numerically in a previous paper [6].

3. Insulators and complex shapes

PIII treatment of insulating materials such as polymers has attracted much interest in recent years. Polymer surfaces can be hardened and made more wear resistant by ion implantation. They may also be coated with metallic thin films. The use of PIII during the film deposition dramatically improves adhesion of these films to the polymer substrate.

The insulating nature of the substrates, however, introduces additional difficulties to the PIII process. The dielectric properties of the substrate determine the voltage that initially appears on the surface in contact with the plasma for a given applied bias voltage. As ions are implanted into the surface it charges positively further reducing the voltage on the surface. This reduction in voltage on the surface throughout the duration of the bias pulse leads to a gradual collapse of the sheath and progressively lowers the energy of the ions implanted.

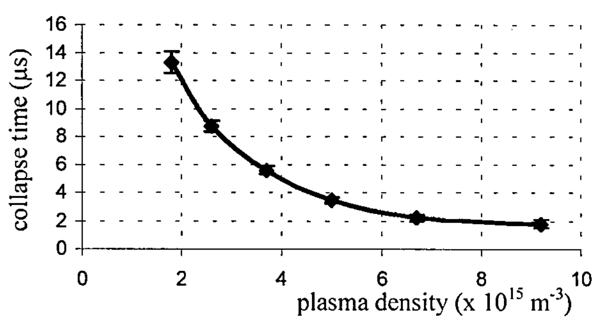

Figure 2: Time for sheath to collapse down to 5 mm as a function of the cathodic arc plasma density at an applied bias of 5 kV as measured by a Langmuir probe.

We have used small Langmuir probes to measure the sheath collapse under a variety of cathodic arc plasma and PIII pulsing conditions. The probe tip was biased to +90 V so that it drew a steady electron current when immersed in the plasma and ceased to draw current when positioned in the electron depleted sheath region.

To investigate the effect of plasma density on the collapse of a sheath around an insulator we placed the probe inside the sheath (5 mm from the substrate surface) and measured the time it took for the sheath to collapse back past the probe for a range of plasma density values. The measured data is plotted, in Figure 2, shows that as the plasma density is increased the time for the sheath to collapse decreases. This indicates that the PIII treatment of insulators is best conducted in plasmas of low density while keeping the applied bias pulse length as low as possible. Because of the finite rise time of the pulse, the use of shorter pulses coupled with the influence of surface charging will enhance the energy spread and low energy ion proportion in the treatment of insulators as compared with conducting substrates.

Practical workpieces such as tools and medical components present further difficulties due to their intricate shapes, particularly associated with points and corners. The equilibrium sheath width in these locations is smaller, making these points more susceptible to electric breakdown. Ion focusing effects also occur making treatments at corners inhomogeneous. These effects need to be better understood and accounted for in further development of practical PIII processing methods.

4. Conclusion

Since its introduction two decades ago, PIII has been shown to be a versatile technique for the surface modification of materials. Aside from its use to for ion implantation, in combination with PVD methods such as cathodic arc deposition, it yields good quality thin film coatings with greatly reduced levels of intrinsic stress and excellent adhesion. There are difficulties associated with the behaviour and dynamics of sheath that occur when employing PIII with insulating substrates and with substrates of complex shape. An improved understanding of the evolution of the sheath will enable the selection of optimum process parameters on a case by case basis.

5. References

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